

Racemic (1,4-dioxan-2-yl)diphenylmethanol

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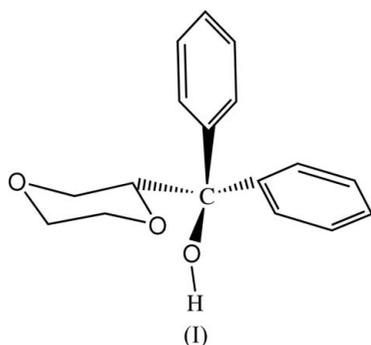
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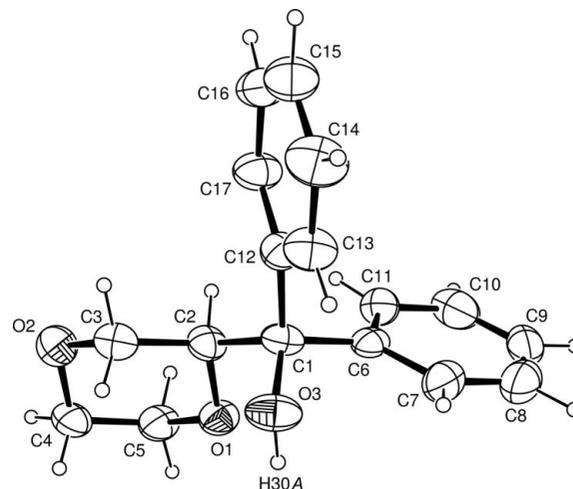
The title compound, $C_{17}H_{18}O_3$, prepared by microwave irradiation of benzophenone and dioxane, crystallizes in a racemic mixture that forms one-dimensional chains *via* strong hydrogen bonding of the hydroxy group to the adjacent symmetry-generated 1,4-dioxan-2-yl group; the O—H...O distance is 1.99 (3) Å and the O—H...O angle is 160 (2)°.

Comment

The formation of C—C bonds is an important synthetic step in organic synthesis, and there are several well known methods that efficiently promote this bond-formation process. One frequently used method involves the coupling of carbon radicals generated during photolysis (Ohkura *et al.*, 2004; Derk *et al.*, 2008), radiolysis (Burr & Strong, 1959), oxidation reactions (Beccalli *et al.*, 2007; Yu *et al.*, 2009) and organometallic catalysed reactions (Hartwig, 2008). The known title compound, (I), was synthesized using microwave irradiation to promote C—C bond coupling between dioxane and benzophenone, and was isolated as a racemic mixture upon crystallization. (I) has been prepared previously by UV irradiation of benzophenone in dioxane, and characterized by 1H and ^{13}C NMR and mass spectrometry (Bakar Bin Baba *et al.*, 1985; Droste *et al.*, 1969). However, to date, no crystal structure of (I) has been reported.



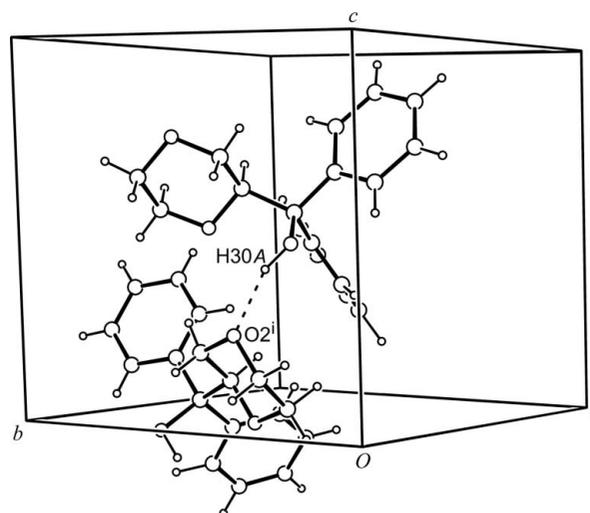
The C—C bond coupling between the 2-position C atom of dioxane and the carbonyl C atom of benzophenone results in the formation of a stereocenter at atom C2. Compound (I)


Figure 1

A view of the *S* enantiomer of (I), showing 50% probability displacement ellipsoids.

crystallizes with one molecule in the asymmetric unit in the noncentrosymmetric space group *Cc*, which was confirmed using the program *PLATON* (routines *ADDSYM* and *NEWSYM*; Spek, 2009). Two enantiomeric forms are present and the structure of the *S* form is shown in Fig. 1. The Hooft analysis parameters $P2(\text{true}) = 1.000$, $P3(\text{true}) = 1.000$, $P3(\text{false}) = 0.000$ and Hooft $y = 0.14(7)$ obtained from *PLATON* were used to assign the absolute configuration (Hooft *et al.*, 2008).

The C—C and C—O bond distances and associated bond angles around atoms C1 [average = 109.04 (17)°] and C2 [average = 109.48 (14)°] are consistent with sp^3 hybridization (Table 1). The C—C and C—O distances, and respective angles, for the phenyl and dioxanyl groups are normal. The phenyl rings adopt a twisted arrangement, minimizing ring-to-ring and H...H atom interactions, while the dioxanyl group adopts a distorted-chair conformation.


Figure 2

A packing diagram for (I), showing the intermolecular hydrogen-bonding interactions between atoms H30A and $O2^i$ of adjacent *S* and *R* enantiomers. [Symmetry code: (i) $x, -y + 1, z - \frac{1}{2}$]

Compound (I) displays intermolecular O—H...O' hydrogen bonding between dioxanyl and hydroxy groups (Desiraju, 1995). A view of the interlinked one-dimensional hydrogen-bonded chain of molecules of (I), projected along the crystallographic *c* axis, is shown in Fig. 2, illustrating the strong hydrogen-bonding interaction, with dimensions as listed in Table 2.

Experimental

The synthesis of (I) and 1,1,2,2-tetraphenylethane-1,2-diol from dioxane and benzophenone has been described in the literature (Droste *et al.*, 1969). Irradiation of a dioxane solution containing benzophenone for 20 h with a mercury arc lamp (340 nm) and a nickel sulfate aqueous filter produces (I) and 1,1,2,2-tetraphenylethane-1,2-diol as the major products. We have prepared (I) by an alternative method using microwave irradiation by the following procedure. Benzophenone (0.55 mmol) was placed in a 125 ml Erlenmeyer flask containing Zn dust (1.02 mmol), ammonium formate (3.96 mmol) and dioxane (5 ml). The reactants were irradiated in a domestic microwave oven (70% power, 1.05 kW) with a heat sink for three periods of 5 min, yielding an amber-colored solution. Excess dioxane was added, the Zn dust was removed by filtration and the filtrate was concentrated by rotoevaporation. Removal of the solvent yielded an amber-colored oil and white crystals. The white solid was the major product. It was easily removed by filtration with a cold methanol wash and was determined to be 1,1,2,2-tetraphenylethane-1,2-diol (m.p. 443–444 K). The amber-colored oil was determined to be a mixture of (I) and several unknown by-products. It was purified by chromatography using a 5:2:1 solution of ethyl acetate–toluene–methanol on silica gel. Compound (I) was crystallized by slow diffusion of toluene, yielding colorless crystals [m.p. 387 K; literature value 388 K (Bakar Bin Baba *et al.*, 1985)]. The ¹H NMR (CDCl₃) spectrum corresponds to that reported in the literature. MALDI-TOF MS: [*M* + H]⁺ 271 *m/z*.

Crystal data

C₁₇H₁₈O₃ *V* = 1398.59 (14) Å³
M_r = 270.31 *Z* = 4
 Monoclinic, *Cc* Cu *Kα* radiation
a = 12.9108 (8) Å *μ* = 0.70 mm⁻¹
b = 10.5408 (5) Å *T* = 100 K
c = 10.3022 (7) Å 0.37 × 0.11 × 0.04 mm
β = 94.016 (6)°

Data collection

Oxford GEMINI CCD area- 4014 measured reflections
 detector diffractometer 2064 independent reflections
 Absorption correction: multi-scan 1805 reflections with *I* > 2σ(*I*)
 (*CrysAlis PRO*; Oxford 2010) *R_{int}* = 0.015
T_{min} = 0.915, *T_{max}* = 0.988

Refinement

R[*F*² > 2σ(*F*²)] = 0.030 Δ*ρ*_{max} = 0.18 e Å⁻³
wR(*F*²) = 0.070 Δ*ρ*_{min} = -0.14 e Å⁻³
S = 1.04 Absolute structure: Hooft *et al.*
 2064 reflections (2008), with 723 Friedel pairs
 251 parameters Flack parameter: -0.2 (2)
 All H-atom parameters refined

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2010); data reduc-

Table 1

Selected geometric parameters (Å, °).

C1—O3	1.418 (2)	C1—C2	1.546 (3)
C1—C12	1.530 (3)	C2—O1	1.417 (2)
C1—C6	1.539 (3)	C2—C3	1.500 (3)
O3—C1—C12	106.56 (16)	O1—C2—C3	110.31 (17)
O3—C1—C6	111.66 (17)	O1—C2—C1	107.07 (17)
C12—C1—C6	107.32 (16)	C3—C2—C1	114.93 (18)
O3—C1—C2	108.80 (17)	O1—C2—H2	106.8 (12)
C12—C1—C2	111.38 (18)	C3—C2—H2	107.4 (12)
C6—C1—C2	111.05 (16)	C1—C2—H2	110.1 (11)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3O <i>A</i> ...O2 ⁱ	0.86 (3)	1.99 (3)	2.813 (2)	160 (2)

Symmetry code: (i) *x*, -*y* + 1, *z* - ½.

tion: *CrysAlis PRO* (Oxford Diffraction, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *ORTEP-3* (Farrugia, 1997), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OV3002). Services for accessing these data are described at the back of the journal.

References

- Bakar Bin Baba, A., Gold, V. & Hibbert, F. (1985). *J. Chem. Soc. Perkin Trans.* 2, pp. 1039–1043.
 Beccalli, E. M., Brogini, G., Martinelli, M. & Sottocornola, S. (2007). *Chem. Rev.* **107**, 5318–5365.
 Burr, J. G. & Strong, J. D. (1959). *J. Phys. Chem.* **63**, 873–876.
 Derk, A. R., Funke, H. H. & Falconer, J. L. (2008). *Ind. Eng. Chem. Res.* **47**, 6568–6572.
 Desiraju, G. R. (1995). *Angew. Chem. Int. Ed.* **34**, 2311–2327.
 Droste, W., Scharf, H. D. & Korte, F. (1969). *Justus Liebigs Ann. Chem.* **724**, 71–80.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Hartwig, J. F. (2008). *Nature (London)*, **455**, 314–322.
 Hooft, R. W. W., Straver, L. H. & Spek, A. L. (2008). *J. Appl. Cryst.* **41**, 96–103.
 Ohkura, K., Ishihara, T., Nakata, Y. & Seki, K.-i. (2004). *Heterocycles*, **62**, 213–216.
 Oxford Diffraction (2009). *CrysAlis PRO*. Version 1.171.33.34d. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
 Oxford Diffraction (2010). *CrysAlis PRO*. Version 1.171.34.36. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.
 Sheldrick, G. M. (2008). *Acta Cryst. A* **64**, 112–122.
 Spek, A. L. (2009). *Acta Cryst. D* **65**, 148–155.
 Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
 Yu, W., Du, Y. & Zhao, K. (2009). *Org. Lett.* **11**, 2417–2420.